歐文日本化學會誌　第一卷第六號

大正十五年六月二十五日印刷
大正十五年六月二十八日發行

編輯兼發行者　東京帝國大學理學部內　松原行一

印刷者　東京市日本橋區兜町二番地　神谷岩次郎

發行所　東京帝國大學理學部內　日本化學會事務所

印刷所　東京市日本橋區兜町二番地　東京印刷株式會社

賣捌所　東京市日本橋區通三丁目十四番地　丸善株式會社

ON THE MECHANISM OF THE SUBSTITUTION REACTION OF TRANS-DICHLORO-DIETHYLENEDIAMINE COBALTIC CHLORIDE IN ITS AQUEOUS SOLUTION.

By Kichimatsu MATSUNO.

Received May 27, 1926. Published July 28, 1926.

Introduction. In the previous paper[1] it has been shown that the chemical changes in aqueous solutions of some cobaltammines could be followed by utilising the valency effect on the coagulation of arsenious sulphide sol. The present investigation was undertaken by the same method, to study the kinetics of the change of trans-dichloro-diethylenediamine cobaltic chloride, $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{Cl}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl}$, in its aqueous solution. It is well known that the aqueous solution of this salt changes its colour gradually from green to violet and finally to red. This colour change is generally considered to be due to the following reactions which take place in the solution,[2]

$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{Cl}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl} + \mathrm{H_2O} \longrightarrow \left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl_2}$$

(I) green (II) violet

$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl_2} + \mathrm{H_2O} \longrightarrow \left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}\ (1)\\ \mathrm{H_2O}\ (2)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl_3}$$

(III) red

As seen in the above formulae, the substitution of chlorine atoms by water molecules in the complex radicals causes not only the colour change but also the increase of the valency of the complex ions of the salts thus produced. The substitution reactions above mentioned may, therefore, be easily followed by observing the colour change as well as the electrolytic conductivity of the solution,[3] and also by means of the coagulation of arsenious sulphide sol.

The last method consists in measuring from time to time the limiting concentrations of the solution which just failed to produce any perceptible

(1) K. Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo*, Vol. 41, Art. 11 (1921).

(2) Werner, *Ann. Chem.*, 386 (1912), 54.
Y. Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, Vol, 37, Art. 2 (1915), 25.
K. Matsuno, ibid., Vol. 41, Art. 10 (1921), 19.

(3) Compare Werner and Herty, *Z. physik. Chem.*, 38 (1901), 341; Lamb and Marden, *J. Am. Chem. Soc.*, 33 (1911), 1787.

coagulation of arsenious sulphide sol within five minutes. The present experiments were carried on with the same sample of arsenious sulphide sol as in the former experiment, so that the empirical formula previously deduced could be used in the following calculations without any transformation. It will be seen that the limiting concentrations thus measured are related to the actual concentrations of the complex salts in the solution and from the sequel the velocity constants of the substitution reactions can be calculated.

Theoretical. As regards to the concentrations of each salt in the solution of $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}$, which were very difficult to estimate, they could be connected with the limiting concentrations by the following consideration.

Let the concentrations of (I), (II) and (III) at the time t be C_A, C_M and C_B respectively, the velocities of decreasing of the first salt and increasing of the last salt will be :

$$\frac{-dC_A}{dt}=k_1C_A \quad \cdots\cdots(1)$$

$$\frac{dC_B}{dt}=k_2C_M \quad \cdots\cdots(2)$$

The velocity of the formation of the intermediate salt is :

$$\frac{dC_M}{dt}=-\frac{dC_A}{dt}-\frac{dC_B}{dt} \quad \cdots\cdots(3)$$

By integration, C_A, C_M and C_B can be obtained as follows :

$$\left.\begin{aligned} C_A&=C_{0A}e^{-k_1t}\\ C_M&=C_{0A}\frac{k_1}{k_2-k_1}\left(e^{-k_1t}-e^{-k_2t}\right)\\ C_B&=C_{0A}\frac{k_1k_2}{k_2-k_1}\left(\frac{1}{k_2}e^{-k_2t}-\frac{1}{k_1}e^{-k_1t}\right)\end{aligned}\right\} \quad \cdots\cdots(4)$$

where C_{0A} denotes the initial concentration and is equal to the sum of C_A, C_M and C_B.

In the substitution reaction in question, the limiting concentration is denoted by S which was assumed to be related to each other as below :

$$S_1\times\frac{C_A}{C_{0A}}+S_2\times\frac{C_M}{C_{0A}}+S_3\times\frac{C_B}{C_{0A}}=S \quad \cdots\cdots(5)$$

S_1, S_2 and S_3 represent the values corresponding to the monovalent, divalent and trivalent cations respectively.

This assumption implies the fact that the coagulation of the sol by the electrolytes is purely an adsorption phenomenon.

In the previous paper (loc. cit.), it was shown that the relation between the valency of the complex radicals of the cobaltammines and their coagulating power on arsenious sulphide sol may be expressed by the following equation :

$$S_n = S_1 \times \frac{1}{N^4} \quad \cdots\cdots(6)$$

where S_n is the limiting concentration (eq. mol) of an N-valent complex ion. Combining (5) with (6), we obtain

$$C_A + \frac{1}{2^4} C_M + \frac{1}{3^4} C_B = \frac{C_{0A}}{S_1} S \quad \cdots\cdots(7)$$

Eliminating the term of the concentrations by the substitution of (4) in (7), we get the following equation :

$$\frac{S-S_3}{S} = 1 - \frac{1}{k_1-k_2}\left(\frac{k_1}{2^4} - \frac{k_2}{3^4}\right)e^{-k_1 t} + \left(\frac{1}{2^4} - \frac{1}{3^4}\right)\frac{k_1}{k_1-k_2} e^{-k_2 t} \cdots\cdots(8)$$

Since S_1 and S_3 were known in the previous experiment, the equation (8) may be solved, if we could determine k_1 and k_2.

In order to determine these velocity constants, the initial and the last state of the reaction were considered. In the beginning of the reaction, we can assume $C_A + C_M = C_{0A}$ neglecting C_B which will be very small compared with C_A and C_M.

The velocity of decaying of the starting substance is

$$-\frac{dC_A}{dt} = k_1 C_A.$$

Now combining the following two equations

$$C_A + C_M = C_{0A}$$

$$S_1 C_A + S_2 C_M = C_{0A} S$$

we get

$$(S_1 - S_2) C_A = C_{0A}(S - S_2)$$

or

$$C_A = \frac{C_{0A}}{S_1 - S_2}(S - S_2).$$

Then, by the integration of the above mentioned velocity equation, we get

$$C_A = C_{0A} e^{-k_1 t}$$

and by the substitution,

$$\frac{S-S_2}{S_1-S_2} = e^{-k_1 t}.$$

Using the common logarithm,

$$k_1=\frac{2.303}{t}\log\frac{S-S_2}{S_1-S_2} \quad \cdots\cdots (9)$$

By the equation (9), k_1 was now calculated as below, taking $S_1=56$ and $S_2=20$.

TABLE 1.

Time (min.)	$S\times 60000$	k_1	mean
22.5	48	0.0111	0.011
56.0	40	0.0105	
92.0	30	0.0139	
120.5	20	0.172	

In the next calculation, the mean value of the first two of the third column in Table 1, namely $k_1=0.011$, was taken.

In the last stage of the substitution reactions, it is expected that there remains so small quantity of the trans-dichloro-diethylenediamine cobaltic chloride that it can be neglected as compared with those of the intermediate and the final salts. A quite similar method of computation can be applied to determine k_2, which is formulated as follows:

$$C_M+C_B=C_{0A}$$

$$S_2C_M+S_3C_B=C_{0A}S$$

$$(S_3-S_2)C_B=C_{0A}(S-S_2)$$

$$C_B=\frac{C_{0A}}{S_3-S_2}(S-S_2)$$

$$\frac{dC_B}{dt}=k_2(C_M-C_B).$$

By integration

$$-\ln\frac{C_{0A}}{S_2-S_3}(S-S_3)=k_2t+\text{const.}$$

$$\ln\frac{S'-S}{S''-S_3}=k_2(t''-t')$$

or

$$k_2=\frac{2.303}{t''-t'}\log\frac{S'-S_3}{S''-S_3} \quad \cdots\cdots (10)$$

Table 2 shows the values of k_2, the mean of which, $k_2=0.0031$, was taken in the further calculation.

TABLE 2.

Time (min.)	$(S-S_3)\times 60000$	$t''-t'$	k_2
120.5	20	507	0.00317
154	16	473	0.00293
193	15	434	0.00304
259	13	368	0.00319
382	9	245	0.00330
507	6	120	0.00337
627	4	—	—

Now that $k_1=0.011$ and $k_2=0.0031$ had been determined, the equation (8) has been solved as below:

$$\frac{S-S_3}{S_1}=0.918\ e^{-0.011t}+0.0698\ e^{-0.0031t} \quad \cdots\cdots(11)$$

Experimental. The method of determining the limiting concentration was entirely the same as in the previous case (loc. cit.) One c.c. of the sol was placed in each of ten carefully cleaned test-tubes of Jena glass which were kept in a thermostat regulated to be 25°C. A certain amount of the salt solution, kept in the same temperature, was taken out, from time to time and each set of the solutions of different dilutions were quickly prepared. Two c.c. of them were added to each of one c.c. of the sol. During addition, the tube were vigorously shaken to ensure thorough mixing. In this way two such concentrations were obtained that the lower did not show any perceptible coagulation whereas the higher did. This concentration was then more carefully examined if necessary and thus the limiting concentration was determined.

(1) (6) Dichloro-diethlenediamine cobaltic chloride, $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}$, which was used in this study was freshly prepared.[1] From the nature of this kind of experiments, an accuracy of high grade could not be expected. In Table 3, S (calc.) denotes the limiting concentration calculated by the equation (11), which could be compared with S (obs.). The theoretical values were fairly well concordant with the experimental. (See Table 3 and Fig. 1).

(1) Joergensen, *J. prakt. Chem.*, (2) 39 (1889), 16.

TABLE 3.

Time (min.)	S (obs.)	S (calc.)
0	$56\times\frac{1}{60000}$	—
22.5	48 „	$51.8\times\frac{1}{60000}$
56	40 „	39.1 „
92	30 „	29.6 „
120.5	24 „	24.3 „
154	20 „	19.9 „
193	19 „	16.3 „
259	17 „	12.7 „
382	13 „	10.0 „
507	10 „	9.0 „
627	8 „	8.6 „

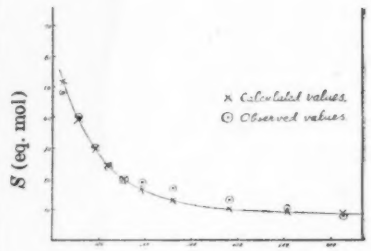


Fig. 1. Time (min.)

As regard the intermediate compound, $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{matrix}\ \mathrm{en_2}\right]\mathrm{Cl_2}$, its concentration will become maximum, when

$$\frac{dC_M}{dt}=0$$

or

$$C_{0A}\times\frac{k_1}{k_2-k_1}\left(k_2\,e^{-k_2t}-k_1\,e^{-k_1t}\right)=0$$

Replacing $k_1=0.011$, $k_2=0.0031$ and equating $k_2e^{-k_2t}-k_1e^{-k_1t}=0$, we could easily find the time when the concentration of $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{matrix}\ \mathrm{en_2}\right]\mathrm{Cl_2}$ was maximum. Namely,

$$t=\frac{2.303}{0.0079}(\log 0.011-\log 0.0031)=160.^{\text{min.}}$$

The second differential of C_M, d^2C_M/dt^2, is equal to

$$C_{0A}\,\frac{k_1}{k_2-k_1}\left(k_1^2e^{-k_1t}-k_2^2e^{-k_2t}\right).$$

At the point where $d^2C_M/dt^2=0$, we find an inflexion point, the time of which could be calculated as below :

$$t=\frac{2.303\times2\,(\log k_1-\log k_2)}{k_1-k_2}=320.^{\text{min.}}$$

Similarly the inflexion point on the velocity curve of the final product of the substitution reactions could be computed thus :

$$\frac{d^2C_B}{dt^2}=\frac{C_{0A}k_1k_2^2}{k_2-k_1}e^{-k_2t}-\frac{C_{0A}k_1^2k_2}{k_2-k_1}e^{-k_1t}=0$$

or $$k_2\,e^{-k_2t}=k_1\,e^{-k_1t}$$

Substituting $k_1=0.011$ and $k_2=0.0031$, we get $t=160^{\text{min.}}$

The inflexion point of C_B curve coincide with the maximum point of C_M curve. (See Fig. 2).

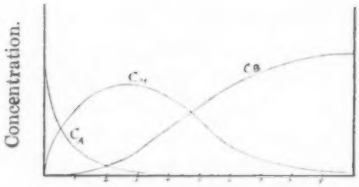


Fig. 2. Time (hour)

Summary.

1. By means of the coagulation of arsenious sulphide sol, the mechanism of the substitution reactions,

$$\left[\text{Co}\begin{matrix}\text{Cl (1)}\\ \text{Cl (6)}\end{matrix}\text{en}_2\right]\text{Cl}\xrightarrow[\text{aq}]{}\left[\text{Co}\begin{matrix}\text{Cl (1)}\\ \text{H}_2\text{O (6)}\end{matrix}\text{en}_2\right]\text{Cl}_2\xrightarrow[\text{aq}]{}\left[\text{Co}\begin{matrix}\text{H}_2\text{O(1)}\\ \text{H}_2\text{O(2)}\end{matrix}\text{en}_2\right]\text{Cl}_3$$

has been studied, and it has been proved that this change is a monomolecular successive reaction.

2. The velocity constants of the first and second reaction of the substitution above mentioned has been calculated as $k_1=0.011$ and $k_2=0.0031$.

3. The time when the intermediate compound would be in its maximum concentration could be computed.

The author is indebted to Prof. Yuji Shibata for his kind advice and to Mr. Haruto Tsukamoto, professor of chemistry in the Hamamatsu Technical High School, for his kind assistance.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

A STUDY OF THE RECIPROCAL SALT PAIR: $[K_2, (NH_4)_2]-[SO_4, CrO_4]$ AT 25°C.

By **Tadashi ISHIKAWA.**

Received May 27, 1926. Published July 28, 1926.

In a systematic study of a reciprocal salt pair, it is necessary to know the solubilities of the four single salts and the equilibria of the systems of two salts with a common ion and water, previous to the study of the

equilibrium of the system in question. In the present case of $[K_2, (NH_4)_2] - [SO_4, CrO_4]$, the necessary data for those equilibria are found in literature.[1] As to the systems of two salts with a common ion, the following facts are to be remarked, all being observed at 25°. Potassium sulphate and potassium chromate, and ammonium sulphate and potassium sulphate form a complete series of solid solutions under the liquid solutions respectively, with no gap. Ammonium chromate and ammonium sulphate, and ammonium chromate and potassium chromate form each two series of solid solutions with a gap. The gaps are respectively 2.90–21.50 and 16.75–55.50 in molar percentage of ammonium chromate.

Materials. The four salts were "extra pure" preparations of E. Merck and have been tested for their purity according to Merck's "*Prüfung der chemischen Reagenzien auf Reinheit.*" Ordinary distilled water was used.

Methods of Analysis. The chromate was estimated by the ordinary method of iodometry. The ammonium was determined by distillation of the sample with caustic soda into a known volume of a standard sulphuric acid and titrating back the excess of the acid with a standard alkali solution, using methyl orange as indicator. The sulphate was determined as barium sulphate. The potassium and water were found by difference.

Experimental Procedure. The experiments were carried out in the following way. Into a solution in equilibrium with two kinds of solid solutions of two salts having a common ion, another salt was added in different proportions and in such an amount that, when the equilibrium was attained, two or three solid phases remained as residue. The mixture in an Erlenmeyer flask of a capacity of about 30 c.c. was made to rotate in a thermostat at 25.0° for at least two days. When the equilibrium was attained, the flask was allowed to stand still in the same thermostat until the suspended matter had settled. Then about 5 c.c. of the solution were taken out by a pipette through a cotton filter into a weighing bottle and subjected to analysis.

---

(1) Single salts: Landolt-Börnstein-Roth-Scheel, "Physikalische Tabellen"; Comey, "Dictionary of Chemical Solubilities of Inorganic Compounds"; Seidell, "Solubilities of Inorganic and Organic Compounds." As to the solubility of ammonium chromate at 25° it is 33.62 grams per 100 grams water, according to Araki (*Mem. Coll. Sci. Kyoto Imp. Univ.*, (A) **8**, No. 3 (1925)), but the writer has found it to be 39.60.

The system of potassium sulphate, potassium chromate and water: Fock, Seidell's "Solubilities," 2d. ed. p. 559; M. Amadori, "Tables annuelles de constantes et données numériques" **3**, 341.

The system of ammonium sulphate, potassium sulphate and water: Fock, Seidell's "Solubilities," 2d. ed. p. 556.

The systems of ammonium chromate, potassium chromate and water, and of ammonium chromate, ammonium sulphate and water: S. Araki, loc. cit.

The composition of the solution was represented by the formula:

$$100m\ H_2O{\cdot}x(NH_4)_2{\cdot}(100-x)K_2{\cdot}y(SO_4){\cdot}(100-y)CrO_4$$

and it was graphically represented by using a square diagram after E. Janecke.[1]

When it was crystallographically confirmed by a Zeiss polarising microscope that there were two phases in the residue, they were separated from the solution by a centrifugal filter machine and then the two kinds of solid solutions mechanically separated from each other as completely as possible.

The two kinds of residues, each of which contained a little of the other and also some of the mother liquor, were analysed. As the pure residues are anhydrous, the amount of the mother liquor adhereing to them was easily calculated from the amount of water contained in the impure residues. The compositions of the anhydrous impure residues were represented by the formula:

$$x(NH_4)_2{\cdot}(100-x)K_2{\cdot}ySO_4{\cdot}(100-y)CrO_4$$

and plotted in the square diagram. Then the points representing the pure solid phases must lie on the extension of the line connecting the two points. Thus, to find the composition of each of the pure solid phases, the materials were mixed in such calculated proportions that when the equilibrium was reached, the liquid solution of the same composition as above was in equilibrium with only one solid phase having its position on the extension line. When such a mixture attained its equilibrium, the residue was microscopically examined and when the residue was found not to be homogeneous, the experiment was repeated with somewhat modified proportions of the materials. This process was repeated until only one solid phase was detected and then it was taken as one of the solid phases in equilibrium with the given liquid solution.

The results are given in the following table and graphically represented in Fig. 1.

No.	Liquid solution.			Solid solution.			
				A.		B.	
	m	x	y	x	y	x	y
1	9.71	100.00	91.44	100.00	97.10	100.00	78.50
2	10.64	91.51	79.37	73.75	92.29	98.28	11.88
3	12.46	88.12	69.32	42.14	88.89	96.72	11.37
4	14.85	77.30	41.15	24.15	84.93	92.86	9.39
5	14.85	66.05	21.29	21.07	77.32	89.86	7.17
6	15.01	59.51	14.19	17.57	71.66	69.42	6.40
7	15.08	52.04	9.79	37.56	41.41	60.20	9.38
8	15.71	42.61	7.59	37.41	14.61	48.16	7.83
9	15.24	45.17	3.63	—	—	49.76	3.30
10	16.82	61.66	0.00	16.76	0.00	55.50	0.00

(1) *Z. anorg. Chem.*, **51** (1906), 132.

The liquid solutions represented by the points on the curve CC′ have always two kinds of solid solutions as the residue which are represented by the points on the lines AA′ and BB′. The crosses on the diagram represent some mixtures of two solid phases and served to find the compositions of the single solid solutions, as above stated.

Fig. 2 represents a model of this system.

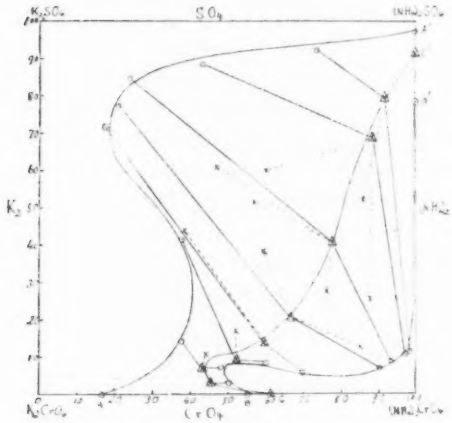


Fig. 1.

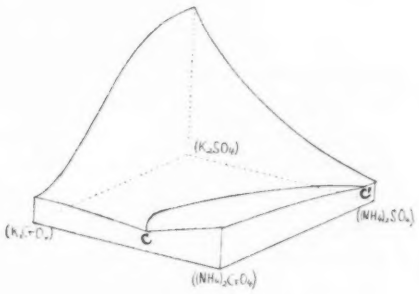


Fig. 2.

Summary.

The equilibrium of the reciprocal salt pair $[K_2, (NH_4)_2]-[SO_4, CrO_4]$ was studied at 25°.

There exist two complete series of solid solutions in equilibrium with liquid solutions.

The compositions of the solid solutions have been determined by a special method.

The equilibrium of the system has been graphically represented using Janecke's square diagram.

In conclusion the writer wishes to express his sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instructions.

Chemical Institute, Faculty of Science,
Kyoto Imperial University.

ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. PART IV. ANOMALOUS DISPERSION AND DEBYE'S DIPOLE THEORY.

By San-ichiro MIZUSHIMA.

Received May 28, 1926. Published July 28, 1926.

A short discussion of the results obtained in the previous experiments[1] will be given in the present paper. According to Debye,[2] abnormally large values of the dielectric polarization observed in the static field as well as for long electric waves are to be ascribed to the orientation of a molecule which has a permanent dipole in it. The polarization being practically constant for a considerably wide range of frequency, the molecule must adapt itself to the change of the external field and manifest fully its dipole moment when the frequency is not very great. To the rotation of a molecule, however, there must exist a resistance which depends upon the internal friction and the dimension of the molecule. Therefore when the frequency of the external field attains a certain value, the molecule will not have time enough to arrange itself in order to exhibit fully its static moment. This must be the cause of the decrease of dielectric constants observed in the previous experiments. When the frequency is still increased, the molecule can hardly adapt itself to the external frequency and the effect of dipole to the dielectric polarization will almost disappear. This is the case for the value of dielectric constants of glycerine, amyl and isobutyl alcohols observed at lower temperatures.

Debye[3] treated this phenomenon theoretically and derived the following equation.

$$\varepsilon = \left\{ \frac{\left(\frac{\varepsilon_0}{\varepsilon_0+2}\right)^2 + \frac{\omega^2\rho^2}{k^2T^2}\left(\frac{\varepsilon_\infty}{\varepsilon_\infty+2}\right)^2}{\left(\frac{1}{\varepsilon_0+2}\right)^2 + \frac{\omega^2\rho^2}{k^2T^2}\left(\frac{1}{\varepsilon_\infty+2}\right)^2} \right\}^{\frac{1}{2}} \cos^2\frac{\varphi}{2}$$

where

$$\tan\varphi = \frac{\omega\rho}{kT}\,\frac{\varepsilon_0+2}{\varepsilon_\infty+2}\,\frac{1-\frac{\varepsilon_\infty}{\varepsilon_0}}{1+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{\varepsilon_0+2}{\varepsilon_\infty+2}\right)^2\frac{\varepsilon_\infty}{\varepsilon_0}}, \qquad \rho = 8\pi\eta a^3.$$

(1) This journal, **1** (1926), 47 83 & 115.
(2) Debye, *Physik. Z.*, **13** (1912), 97.
(3) Debye, *Verh. Deut. physik. Ges.*, **15** (1913), 770.

ε is the dielectric constant observed in the alternating field, the frequency of which is $\frac{\omega}{2\pi}$; ε_0 the static dielectric constant; ε_∞ the dielectric constant at the frequency at which the effect of dipole disappears; η the viscosity; a the radius of molecule; T the absolute temperature and k Boltzmann's constant. Among the data necessary for the calculation of ε of monovalent alcohols, ε_0 is known from the study of Abegg and Seitz[1] and ε_∞ from the refractive indices for visible light.[2] The most rational value of a can be obtained by the kinetic theory from the viscosities in the gaseous state. But this method is available only for ethyl alcohol.[3] For homologous series of alcohols a^3 can be assumed to be proportional to b in van der Waals' equation. The values of a for other alcohols can, therefore, be calculated from a for ethyl alcohol and b given in Landolt-Börnstein's Tables.[4] The viscosities of alcohols at low temperatures were recently measured by Mr. Yoshizaki in our institute. Thus we have all data necessary for the calculation of ε. The calculated values of ε ($\varepsilon_{cal.}$) and those observed at the wave length of 9.5 metres ($\varepsilon_{obs.}$) are shown in the following tables.

	Ethyl Alcohol $a=1.8\times10^{-8}$ cm.					Propyl Alcohol $a=2.0\times10^{-8}$ cm.				
Temp.	ε_0	ε_∞	η	ε_{cal}	ε_{obs}	ε_0	ε_∞	η	ε_{cal}	ε_{obs}
20	25.8	1.85	0.0119	26	25	22.2	1.92	0.0226	22	22
10	27.0	1.86	0.0145	27	27	23.5	1.94	0.0292	23	23
0	28.4	1.88	0.0177	28	28	24.8	1.95	0.0388	24	25
−10	30.3	1.90	0.0218	30	30	26.2	1.97	0.0513	24	25
−20	32.0	1.91	0.0276	31	31	27.5	1.98	0.0716	22	24
−30	33.7	1.92	0.0358	32	33	29.0	2.00	0.103	19	20
−40	35.3	1.94	0.0490	31	33	30.5	2.02	0.154	14	15
−50	37.6	1.96	0.0684	29	29	32.0	2.03	0.236	9	10
−60	39.7	1.98	0.0959	25	24	33.7	2.05	0.386	6	7

(1) Abegg and Seitz, *Z. physik. Chem.*, **29** (1899), 242.

(2) The square of the refractive index for D line were taken as ε_∞, disregarding the inversion of spectrum in the infra-red region.

(3) Landolt-Börnstein "Tabellen" (1923).

(4) b for amyl alcohol can be extrapolated on the assumption that b is additive for homologous series.

	Isobutyl Alcohol $a=2.0\times10^{-8}$ cm.					Amyl Alcohol $a=2.1\times10^{-8}$ cm.				
Temp.	ε_0	ε_∞	η	ε_{cal}	ε_{obs}	ε_0	ε_∞	η	ε_{cal}	ε_{obs}
20	20.0	1.95	0.0391	19	19	16.0	1.98	0.0437	16	16
10	21.0	1.97	0.0555	20	20	16.8	2.00	0.061	16	18
0	21.8	1.99	0.0804	19	20	17.5	2.02	0.0876	15	17
−10	23.2	2.00	0.116	17	17	18.6	2.03	0.130	13	15
−20	24.5	2.02	0.182	13	11	19.7	2.05	0.207	9	10
−30	25.7	2.03	0.30	8	7	20.8	2.07	0.33	6	7
−40	27.0	2.05	0.56	4	5	21.8	2.08	0.58	4	5
−50	29.0	2.07	1.14	3	4	23.0	2.10	1.01	3	4

It can now be admitted that Debye's theory holds in the first approximation for monovalent alcohols. The discussion on glycerine will be given in the following papers which will also contain the results measured at different wave lengths.

The author wishes to express his best thanks to Prof. M. Katayama for his kind guidance.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

ETUDES DE DÉRIVÉS DU FURFURAL.
II. ETUDES SPECTROGRAPHIQUES DE QUELQUES CÉTONES FURYLIQUES.

Par **Itizo KASIWAGI.**

Reçu le 11 mai 1926. Publié le 28 juillet 1926.

Dans un premier mémoire[1] nous avons mentionné que nous avions réussi à préparer de nouvelles cétones furyliques. Ces cétones présentent des propriétés optiques très remarquables ; —exaltation de la réfraction moléculaire, comme nous en avons déja signalée, coloration intense à l'action des alcalis, pouvoir absorbant des rayons ultraviolets, etc. C'est l'étude spectrographiques de la relation entre l'absorption et la constitution des cétones.

(1) Kasiwagi, Ce journal, **1** (1926), 90.

Toutes les cétones étudiées renferment dans leurs molécules au moins un noyau furanique, $\begin{matrix} C=C-C=C \\ |\_\_\_O\_\_\_| \end{matrix}$, qui constitute leur chromophore principale. Ce chromophore semble un faible absorbeur de rayons, car le furfurane $\begin{matrix} CH=CH-CH=CH \\ |\_\_\_\_\_O\_\_\_\_\_| \end{matrix}$ en solution alcoolique ne donne pas absorption séléctive ni dans la région visible ni dans la région ultraviolette,[1] mais, lorsqu'il est combiné avec un autre chromophore, il devient presque sans exception un chromogène très puissant. Par légère alourdissement de la molécule absorbante, une bande d'absorption apparaît dans la régien ultraviolette. Nous avons pu constater ce fait par le furylcarbinol (I), qui, malgré son faible pouvoir absorbant, donne une bande à $\lambda=267\mu\mu$ environ. Cette absorption n'a lieu qu'en solution assez concentrée (1/10 N), comme on le voit plus loin.

L'absorption du furfural a fait l'objet d'études assez nombreuses. Hartley et Dobbie examinèrent les solutions alcooliques de furfural (aux divers concentrations) et ne purent trouver aucune bande d'absorption.[2] Cependent il est douteux qu'il n' en possède pas de tout, lors même le furylcarbinol (I) absorbe séléctivement.

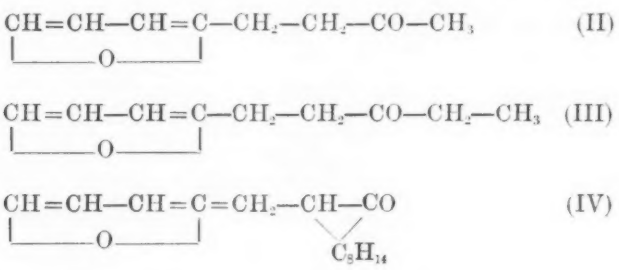
$$\begin{matrix} CH=CH-CH=C-CH_2OH \\ |\_\_\_\_\_O\_\_\_\_\_| \end{matrix} \qquad \text{(I)}$$

En 1910 Purvis étudia l'absorption du furfural à l'état de vapeur et en solution, et trouva que la solution alcoolique à 1/1000 N absorbe près de $\lambda=270\mu\mu$ à l'épaisseur 2 mm. de la couche de la solution.[3] Plus tard Bielecki et Henri étudièrent la même absorption quantitativement, et trouvèrent deux bandes, dont les maxima se trouvent à $\lambda=268\mu\mu$ (bande principale) et à $\lambda=334.5\mu\mu$.[4] Tout récemment Getman a reprit cette étude, et il a constaté que l'aldéhyde possède une bande, dont le maximum se trouve à $\lambda=270\mu\mu$.[5]

Cette bande à $\lambda=270\mu\mu$ environ, est-elle attribuée au noyau furanique seul ou au groupement furfurylidénique $\begin{matrix} -C=C-C=C-C= \\ |\_\_\_O\_\_\_| \end{matrix}$, c'ést-à-dire au noyau furanique plus une double liaison éthylénique (la double liaison entre C et O du groupe carbonyle) en position conjuguée avec une dans le noyau ?

(1) Purvis, *J. Chem. Soc.*, **97** (1910), 1655.
(2) Hartley et Dobbie, *J. Chem. Soc.*, **73** (1898), 598.
(3) Purvis, loc. cit.
(4) Bielecki et Henri, *Ber.*, **47** (1914), 1690.
(5) Getman, *J. Phys. Chem.*, **28** (1924), 397.

Les cétones furyliques avec une chaine latérale saturée, telles que la furylbutanone (II), la furylpentanone (III) et le furfurylcamphre (IV),



possèdent une bande exactement en même position, comme suit :

TABLE 1.

	Position du maximum de la bande[1]
Furylbutanone	$\lambda = 266\mu\mu$
Furylpentanone	268
Furfurylcamphre	266
Furylcarbinol	268

Dans ces cas, quoique les constitutions des composés cités diffèrent considérablement les unes des autres, ils donnet une bande à la même position $\lambda = 267\mu\mu$. Il est tout à fait remarquable que l'alcool renferme le même chromophore que celui du furfurane, et donne une bande à la même position. Par conséquent on peut conclure que le groupe carbonyle des cétones citées, ainsi que celui du furfural, n'influe pas du tout sur la position de l'absorption du noyau furanique.

Cependant le groupement carbonyle présente toujours plus ou moins un effet chromatique. On peut voir ce fait dans la Table 2. (pour construire cette table on calcule de chaque observation, les épaisseurs minima des bandes à la même con-

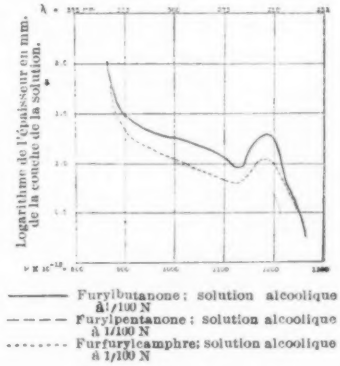

Logarithme de l'épaisseur en mm. de la couche de la solution.
Furylbutanone ; solution alcoolique à 1/100 N
Furylpentanone ; solution alcoolique à 1/100 N
Furfurylcamphre; solution alcoolique à 1/100 N

Fig. 1.

(1) Les valeur sont simplement moyens arithmétiques des longueurs d'onde aux deux extrémités des bandes d'absorption aux épaisseurs les plus minces.

centration dite 1/10000 N d'après la lois de Beer, c'est-à-dire

$$c.\ d = \text{constant},$$

où c = concentration et d = épaisseur de la couche de la solution) :

TABLE 2.

	Epaisseur de la couche la plus mince de chaque solution à 1/10000N où l'absorption paraît.
Furylbutanone	900 mm.
Furylpentanone	700
Furfurylcamphre	700
Furylcarbinol	20000
Furfural	20

Ces chiffres étant naturellement inversement proportionnels aux coéfficients d'absorption, le furylcarbinol est le plus transparent aux rayons ultraviolets, tandis que le furfural est le plus opaque. On peut conclure que, dans le cas du furfural, qui possède deux fois les doubles liaisons conjuguées, en tenant la double liaison intremédiaire en commun

le groupe carbonyle influe fortement sur le noyau furanique, et en cas des cétones furyliques, qui renferment les mêmes chromophores que le furfural, mais le groupe carbonyle est éloigné du noyau furanique, ainsi perdant une double liaison conjuguée

le même groupement influe assez peu, mais également avec la même intensité.

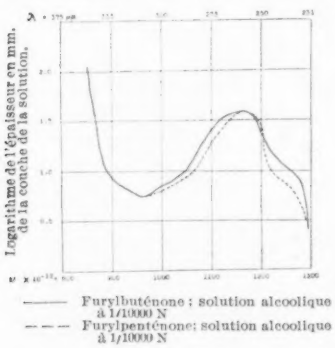

Logarithme de l'épaisseur en mm. de la couche de la solution.
Furylbuténone : solution alcoolique à 1/10000 N
Furylpenténone: solution alcoolique à 1/10000 N

Fig. 2.

En haut nous avons décrit seulement l'effet hyperchrome du groupe carbonyle. On peut en voir en bas l'effet hyperchrome et bathochrome à la fois, par introduction d'une double liaison dans les molécules absorbantes entre le groupe carbonyle et le noyau furanique, formant ainsi un système optique puissant

. La table suivante montre clairement ce fait :

TABLE 3.

	Position de la bande[1]	Epaisseur minimum de la solution à 1/10000 N où l'absorption paraît.
Furylbuténone[2]	$\lambda = 314\mu\mu$	6 mm.
Furylpenténone[3]	311	6
Furyldiméthylpenténone[4]	314	7
Furfuralcamphre[5]	314	8

Ces chiffres indiquent que les cétones non saturées déplacent l'absorption maximum bathochromiquement environ $50\mu\mu$ (c'est-à-dire vers le coté rouge du spectre), et elles absorbent presque 100 fois plus que les cétones saturées correspondentes.

Par cette étude spectrographique nous avons pu constater qu'il existe une relation nette entre l'absorption et la constitution des cétones furyliques.

De plus par augementation du nombre de doubles liaisons l'effet bathochrome se manifeste avec intensité, car la difuryl-1.5-pentadién-1.5-one-3 donne *probablement* deux bandes assez larges. Stobbe et Haertel en ont étudiée l'absorption seulement dans les régions visibles, et conséquemment ils n'ont pas mentionné l'existence des bandes.[6]

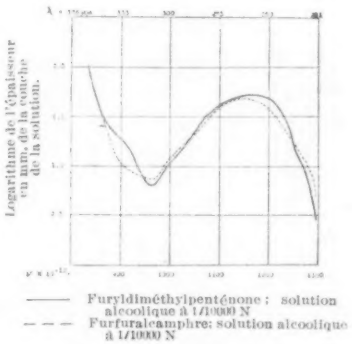

Logarithme de l'épaisseur en mm. de la couche de la solution.
Furyldiméthylpenténone : solution alcoolique à 1/10000 N
Furfuralcamphre: solution alcoolique à 1/10000 N

Fig. 3.

Dans la table ci-dessous nous donnerons une comparaison des groupements phényle et furyle :

(1) Voir (1) la page 147.

(2) $C_4H_3O{\cdot}CH{=}CH{\cdot}CO{\cdot}CH_3$

(3) $C_4H_3O{\cdot}CH{=}CH{\cdot}CO{\cdot}CH_2{\cdot}CH_3$

(4) $C_4H_3O{\cdot}CH{=}CH{\cdot}CO{\cdot}C(CH_3)_3$

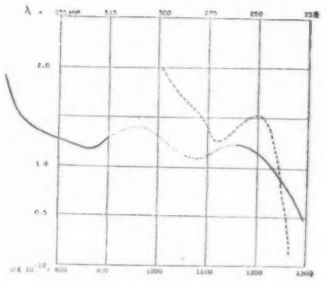
(5) $C_4H_3O{\cdot}CH{=}C(C_8H_{14}){-}CO$

(6) Stobbe et Haertel, *Ann.*, 370 (1909), 99.

TABLE 4.

	Position de la bande	Epaisseur minimum de la solution à 1/10000 N où l'absorption paraît
Benzalcamphre[1]	$\lambda = 290\ \mu\mu$	18 mm.
Furfuralcamphre	314	8
Phénylbuténone[2]	285	7.6
Furylbuténone	314	6

On peut y voir nettement que le noyau furanique est, comme Stobbe et Haertel l'ont remarqué en se bornant dans les régions visibles,[3] plus bathochrome et plus hyperchrome que le noyau benzénique, même dans la région ultraviolette.



—— Difurylpentadiénone : solution alcoolique à 1/10000 N
– – – Furylcarbinol : solution alcoolique à 1/10 N

Fig. 4.

Note Experimentale.

Les cétones furyliques que nous avons étudiées ont été preparées dans notre laboratoire,[4] et elles sont distillées à nouveau avant emploi.

Furylbuténone : p. é. 110–114° sous 10 mm. On pèse exactement 0.001 molécule-gramme, dissout dans de l'alcool dit " alcool absolu Merck " en faisant en 100 c.c. Ainsi on a la solution alcoolique à 1/100 N. Pour obtenir la solution à 1/10000 N on étend 1 c.c. de cette solution à 100 c.c.

Furylpenténone : p. é. 132–135° sous 20 mm.

Furyldiméthylpenténone : p. é. 145–147° sous 35 mm.

Furfuralcamphre : p. é. 165–180° sous 10 mm. Ce corps est préparé d'après le procédé de Mlle. N. Wolf au moyen de l'amidure de sodium.[5]

Difurylpentadiénone : p. f. 57.5–58.5°.[6]

Furylbutanone : p. é. 81° sous 10 mm.

(1) Lowry et Southgate, *J. Chem. Soc.*, 97 (1901), 905. Nous avons calculé ces valeurs, en mettant $1/\lambda = 3450$ et l'épaisseur de la solution à 1/1000 N = 1.8 mm. par interpolation de la courbe donnée par ces auteurs.

(2) Baly et Schaefer, *J. Chem. Soc.*, 93 (1908), 1813. En basant de la courbe donnée, nous avons obtenu $\lambda = 285\mu\mu$ et l'épaisseur minimum de la couche de la solution = 7.6 mm.

(3) Stobbe et Haertel, loc. cit.

(4) I. Kasiwagi, loc. cit.

(5) Mlle. N. Wolf, *Ann chim.*, (9), 20 (1923), 32.

(6) Erdmann, *Ber.*, 35 (1902), 1855.

Furylpentanone : p. é. 88° sous 10 mm.

Furfurylcamphre : p. é. 165° sous 10 mm.[1]

Furylméthanol : p. é. 73.5° sous 15 mm. Préparé d'après le procédé de Erdmann.[2]

Le spectrographe en quartz que nous nous sommes servi est du type E 3 d'Adam Hilger, à Londres, et les plaques photographiques sont l'anti screen, Wellington et Ward.

Comme source lumineuse nous avons employé l'arc entre éléctrodes en fer.[3]

Pour construire les graphiques ci-joints on porte en abscisses les fréquences (ν) multipliées par 10^{-12} et en ordonnées les épaisseurs en mm. des couches des solutions en échelle logarithmique. En employant ν au lieu de $1/\lambda$, on a la relation suivante entre ces quantités :

$$\nu = 3 \times 10^{17}/\lambda$$

où 3×10^{17}est la vitesse de la lumière.[4]

Haute école polytechnique de Yokohama.

STUDIES ON PROTEINS. III.

ACTION OF SUPERHEATED WATER ON PROTEINS. II.[5]

By **Shigeru KOMATSU** and **Chuichi OKINAKA.**

Received May 17, 1926. Published July 28, 1926.

It has been shown in the previous article[6] on this subject, that proteins when subjected to the action of superheated water, were transformed into soluble and insoluble substances which were regarded as the result of reverse reactions—polymerisation or condensation and hydrolysis—which take place simultaneously in the reaction system, and that these reaction products were different with each individual protein from which they were derived, from the study of the elementary analysis and the distribution of nitrogen,

(1) Mlle. N. Wolf, *Ann. chim.*. (9), 20 (1923), 32.

(2) Erdmann, *Ber.*, 35 (1902), 1855.

(3) Nous tenons à remercier bien vivement à M. Y. Shibata, professeur de l'Université de Tokyo, qui a eu l'obligence de nous fournir des éléctrodes.

(4) V. Henri, "Etudes de Photochimie," 1919.

(5) The expenses of this investigation were shared by the Imperial Academy of Japan.

(6) This journal, 1 (1926) 102.

which have no definite chemical compositions, according to the various external conditions under which the proteins were submitted to the chemical action.

For the verification of the above conclusions, the present research on the determination of the P_H value and the buffer action of the individual reaction products from proteins at the various stages of the reaction, was undertaken.

TABLE 1.

Edestin.

Time (in hours) (t)	0		1		2		4		20
Diss. subst. (%) (Q)	0		5.7		15.5		24.7		63.4
$\Delta Q/\Delta t$[1]		5.7		9.8		4.6		2.4	
P_H	6.3		7.3		—		—		6.9

Time (in hours) (t)	0		3		6		9
Quantity of diss. amide nitrogen (Q) (%)	0		25.		49.		53.
$\Delta Q/\Delta t$		25		8		1.3	

Gliadin.

Time (in hours) (t)	0		2		6		15.5
Diss. subst. (%) (Q)	0		5.5		9.9		28.8
$\Delta Q/\Delta t$		2.75		1.1		2.	
P_H	5.7		—		6.37		6.44

Casein.

Time (in hours) (t)	0		2		6		17		20
Diss. subst. (%) (Q)	0		1.34		5.85		14.		
$\Delta Q/\Delta t$		0.67		1.1		0.74			
P_H	4.6		—		4.7		—		5.0

For the determination of the P_H value of the reaction products—the residue and solution,— each protein was heated with water in a stoppered bottle at 120° for one, six, and twenty hours, respectively, and the hydrogen ion concentration of the products was studied by the electrometric method as will be seen in the above table.

(1) ΔQ and Δt denote the difference of Q and t respectively.

The P_H value of the solution from edestin, as may be seen in the table, was increased at the beginning of the reaction and then decreased, whilst that from casein shows a constant increase in the progress of reaction. Although the P_H value in case of gliadin was on the increase with reaction time, which seems apparently to be changed in an analogous manner with that in the case of casein, it should be proper to consider, when we study it precisely, that gliadin behaves toward superheated water partly like edestin and partly like casein, since the rate of increment in the P_H value of the solution from gliadin for a first certain time is greater than that for latter part of the reaction period.

When the P_H value of the reaction products of the proteins was compared with the distribution of nitrogen and especially with their amide nitrogen content (Table 1) it was noticed that some parallelism existed between them, and the vicissitude of the P_H value of the solution with lapse of the reaction time, will be explained well by our hypothes mentioned in the previous article that the compounds containing diamino nitrogen would be transformed partly into those containing the amide nitrogen during the process, and moreover, that the manner in which the protein would be decomposed into fragmentary complex groups, would be a characteristic of the individual protein.

The solution obtained from edestin with water at 120° for twenty hours, having the value of P_H of 6.9, will become cloudy when the P_H of the solution reaches 6 by the addition of acetic acid and the precipitation of a compound vividly took place while the P_H was climbing from 5.3 to 5.0 and completed at P_H of 4.8, accordingly the isoelectric point of the substance was assumed to be $P_H=5.2$, since at that point the affinity of a compound for water is in a relative minimum.(1) The same was noticed with the solution ($P_H=6.4$) which obtained by digestion of gliadin with water for twenty hours; when acetic acid was added gradually to the solution, and the precipitation of a compound occurs when the acidity of the solution has reached to $P_H=6.4$, the vicissitude of its isoelectric point. No flocculation, however, has occurred of the solution of the P_H of 5.0, which was prepared from casein under the same conditions as the other proteins, owing to the P_H of the solution being already on the acid side of the isoelectric point of compounds which were regarded as being formed as cleavage products of the casein molecule, and consequently the so-called residue was considered partly of these cleavage products which remained there, without entering into the solution.

From these facts, we concluded that the constituents of the solutions resulting from the action of the superheated water on proteins, would be as different essentially from each other, as the difference of the individual pro-

(1) W. M. Clark, "The Determ. of Hydrogen Ion Conc." 2nd. ed. (1923), p. 342.

teins in the chemical constituents, which has already been admitted by chemists.[1] Accordingly, the following statement will be borne in mind that the constituents of the insoluble residue, from the study of the P_H value of the soluble substances, would be different from each other, as we stated in the previous article, since the hydrogen ion concentration of a solvent is one of the most important factors controlling the solubility of proteins or amphotelytes of complex nature.[2]

A solution from 2 grams of edestin, by digesting with 40 c.c. of water at 120°, for one hour, and made up to 50 c.c., which was found to have a value of P_H of 7.4. To the solution were added a successively increasing amount of N/25 acetic acid on the one hand, and N/50 sodium hydroxide solution on the other, and the resulting P_H was measured in each case. The P_H values were then plotted as usual and the results were as may be seen in Curve III, in Fig. 1 and Fig. 2. Curve II′, in these figures, was constructed analogously with data obtained with the solution prepared from the protein after digesting for twenty hours under the same conditions. Curve II of the figure were obtained in a similar way of ten times diluted solution of the latter solution. The results show that the buffer action of the solution as we expected from other examples, depended upon the concentration of the constituents. The solution obtained by digestion for twenty hours is much more resistant to change in the P_H than the solution of the same concentration, obtained by digestion for only one hour. These relations were observed to be true also of casein, as will be seen in Fig. 5 and Fig. 6, but of the solution from gliadin, these stochiometrical relations do not hold ; the solutions of the same concentration show the same buffer action though they were prepared under different conditions (Fig. 3 and Fig. 4). That the P_H value of the solution from edestin was decreased from 6.96 to 6.78 when diluted ten times, whilst of its hundred times diluted solution the P_H value was inversely increased to 8.07, are facts worth discussing.

For obtaining more definite knowledge of the occurrence of compounds of complex nature such as albumose or peptone, in the solution which was resulted by digestion of protein, the buffer value of the solution was investigated.

As was supposed from the study of the buffer values (dB/dP_H) of the solutions, differentiated graphically from their titration curve above-mentioned, following the method proposed by D.D. van Slyke,[3] there occur at least two compounds of complex nature in each solution, as will be seen in Fig. 7, 8, 9, 10, 11 and 12, obtained by the action of superheated water on proteins. Such indication of the buffer value for the existence of the compounds will be proved experimentally in the next article by isolating them from the solution.

(1) T. B. Osborne, "The Vegitable Proteins," (1909), p. 59.
(2) Robertson, "Physical Chemistry of Proteins," (1918), pp. 275, 248.
J. Loeb, "Proteins and the Theory of Colloidal Behavior," pp. 243, 266.
L. Michaelis, "Die Wasserstoffionen-Konzentration," (1919), p. 44.
R. H. Bogue, "Colloidal Behavior." (1924), p. 35.
(3) *J. Biol. Chem.*, **52** (1922), 524.

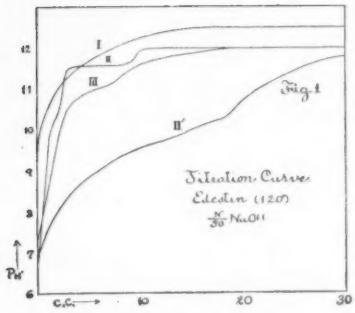


Fig. 1. I: Water.
II: Hydrolized 20 hours (0.25%).
II': Hydrolized 20 hours (2.5%).
III: Hydrolized 1 hour (0.24%).

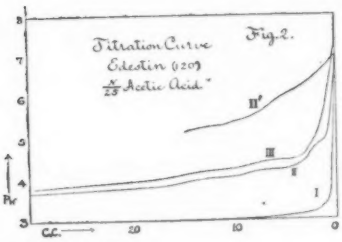


Fig. 2. I: Water.
II: Hydrolized 20 hours (0.25%).
II': Hydrolized 20 hours (2.5%).
III: Hydrolized 1 hour (0.24%).

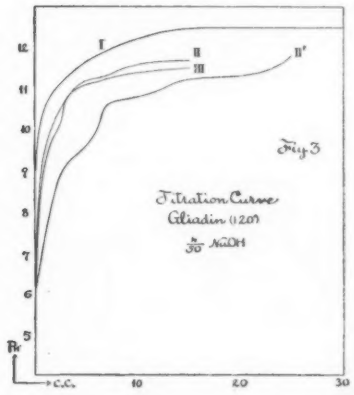


Fig. 3. I: Water.
II: Hydrolized 20 hours (0.4%).
II': Hydrolized 20 hours (1.4%).
III: Hydrolized 6 hours (0.4).

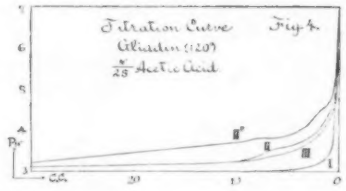


Fig. 4. I: Water.
II: Hydrolized 20 hours (0.4%).
II': Hydrolized 20 hours (1.4%).
III: Hydrolized 6 hours (0.4%).

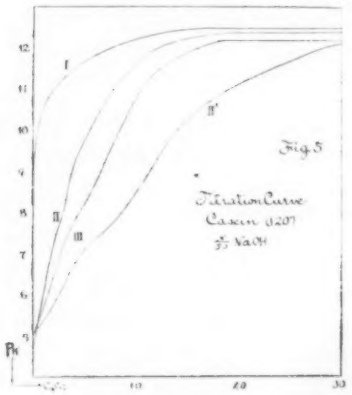


Fig. 5. I: Water.
II: Hydrolized 20 hours (0.24%).
II': Hydrolized 20 hours (0.64%).
III: Hydrolized 6 hours (0.24%).

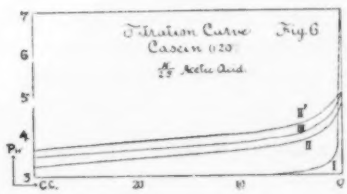


Fig. 6. I: Water.
II: Hydrolized 20 hours (0.24%).
II': Hydrolized 20 hours (0.64%).
III: Hydrolized 6 hours (0.24%).

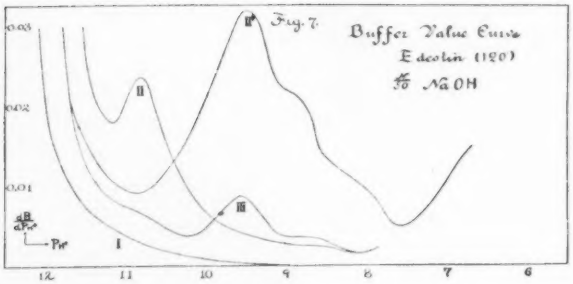


Fig. 7.
I: Water.
II: Hydrolized 20 hours (0.25%).
II': Hydrolized 20 hours (2.5%).
III: Hydrolized 1 hour (0.24%).

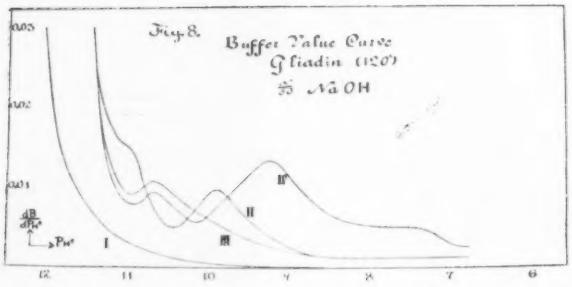


Fig. 8.
I: Water.
II: Hydrolized 20 hours (0.4%).
II': Hydrolized 20 hours (1.4%).
III: Hydrolized 6 hours (0.4%).

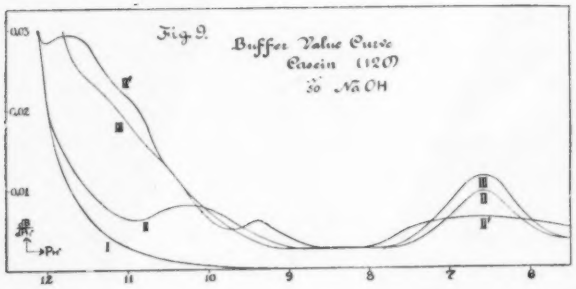


Fig. 9.
I: Water.
II: Hydrolized 20 hours (0.24%).
II': Hydrolized 20 hours (0.64%).
III: Hydrolized 6 hours (0.24%).

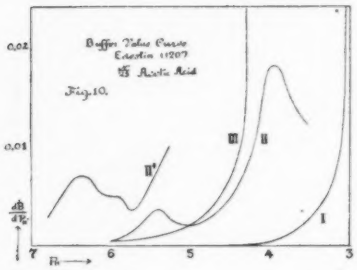


Fig. 10.

I: Water.
II: Hydrolized 20 hours (0.25).
II': Hydrolized 20 hours (2.5%).
III: Hydrolized 1 hour (0.24%).

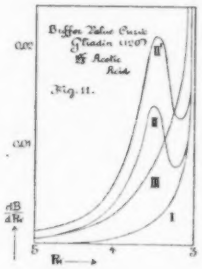


Fig. 11.

I: Water.
II: Hydrolized 20 hours (0.4%).
II': Hydrolized 20 hours (1.4%).
III: Hydrolized 6 hours (0.4%).

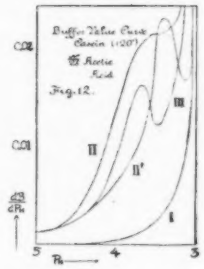


Fig. 12.

I: Water.
II: Hydrolized 20 hours (0.24%).
II': Hydrolized 20 hours (0.64%).
III: Hydrolized 6 hours (0.24%).

November 1924.

Laboratory of Organic and Bio-Chemistry.
Kyoto Imperial University.

ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. I. THE ACTION ON A MIXTURE OF ANILINE AND METHYL ALCOHOL.

By **Harushige INOUE.**

Received May 17, 1926. Published July 28, 1926.

It has already been shown by Mailhe and Godon,(1) and Brown and Emmet(2) that silica and alumina which are the principal components of Japanese acid earth, promote the dehydration of alcohols and also the condensation of alcohols and amines. On repeating these experiments with alumina prepared from ammonium alum obtained from Potter's clay by heating at 700–800° and then treated with concentrated sulphuric acid and ammonium sulphate successively, the same experimental result as obtained by other chemists, was obtained.

When, however, silica, prepared from natural pumice by treating with concentrated nitric acid for several days, and composed of 98.30 percent of

(1) Mailhe and Godon, *Compt. rend.* **160** (1918), 467 & 564.
(2) Brown and Emmet, *J. Am. Chem. Soc.*, **46** (1924), 1836.

SiO_2 and 1.67 percent of Fe_2O_3, was used as catalyst, a result was obtained which differed from others in detail. A mixture of 46 grams of aniline and 18 grams of methyl alcohol was passed over the catalyst heated at 350°, 47.1 grams of reaction product was obtained, which after examination of the physical constants and the melting point of the acetates of fractions yielded by fractional distillation, as will be seen in Table 1, was confirmed as composed of p-toluidine and methylaniline.

TABLE 1.

No.	Fraction	Yield (gr.)	Sp.gr.(d_4^{20})	M.p. of acetate	Principal product
1	90–100°	0.9	—	—	—
2	185–190°	2.9	0.9937	107–111°	Aniline & Methylaniline
3	190–195°	18.1	0.9910	120–122°	Methylaniline & p-toluidine
4	195–198°	6.2	0.9865	124.5–126.5°	Methylaniline & p-toluidine
5	198–202°	4.0	0.9809	132.5–133.8°	p-Toluidine
6	202–210°	2.6	—	129–132°	—
7	210–215°	1.5	—	—	—

p-Toluidine was isolated in the pure form of the acetate (m. p. 146°–147°), from the fifth fraction, b. p. 198–202° shown in Table 1.

The author has, therefore, studied the action of Japanese acid earth on a mixture of methyl alcohol and aniline, and has observed that the condensation of these substances, and the contact isomerisation of the condensed substance have occurred simultaneously.

The catalyst used in the experiment was obtained from crude Japanese acid earth, washed with water, and dried, which gave on analysis the following chemical compositions:

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Moisture dried at 110°	Ignition loss	Total
61.67%	12.28%	1.87%	0.16%	3.44%	15.66%	4.64%	99.72%

The earth was filled in a glass tube of 1 metre in length, and 2 cm. in diameter, heated to 350°, and a mixture of methyl alcohol and aniline was passed on it.

p-Toluidine.

From the reaction product of 22 grams methyl alcohol and 55 grams aniline, 50.4 grams of an oily substance and 17.5 grams of water were obtained, and the oily substance was divided into the following 7 fractions by fractional distillation, and the density of each fraction was determined and

the melting-point of the acetates obtained by treating the oil with acetic anhydride was also determined.

TABLE 2.

No.	Fraction	Yield (gr.)	Sp. gr. (d_{20}^{20})	M.p. of acetate	
				1	2
1	to 180°	2.9	—	—	—
2	189–193°	7.4	0.9977	120–121°	about 125°
3	193–197°	13.4	0.9947	139–143°	140–143°
4	197–200°	11.2	0.9904	140–143°	140–143°
5	200–205°	5.0	0.9858	140–143°	103–106°
6	205–207°	3.3	0.9814	114–116.5°	105–106°
7	Residue	2.8	—	—	—

In the table, acetate 1 and acetate 2 respectively show the melting-point of the first and second crops of crystals, separated from solutions.

The third and fourth fractions which composed the main part of the reaction product, from the melting-point of the acetates, were noticed to be composed principally of p-toluidine. Higher fractions boiling above 200°, should contain, by refering to their physical and chemical properties, some homologous substances of aniline, and other secondary and tertiary amines.

Methylaniline.

When, however, a mixture of 50 grams methyl alcohol and 120 grams aniline was passed in an interval of 8 hours on the catalyst heated to 250°, 106 grams of an oily reaction product and 26 grams of water were obtained, and the reaction product was divided into the following 6 fractions by fractional distillation.

TABLE 3.

No.	Fraction	Yield (gr.)	Sp. gr. (d_{20}^{20})
1	75–100°	—	—
2	180–187°	21.7	1.0051
3	187–190°	25.8	1.0028
4	190–197°	37.8	0.9949
5	197–200°	6.1	0.9852
6	Residue	—	—

The fourth fraction, b. p. 190–197°, was confirmed as consisting of methylaniline, since its density and the melting-point of the acetate agree with those of methylaniline.

To our interest, when an equimolecular mixture of methyl alcohol and aniline was passed on Japanese acid earth heated at 250°, methylaniline was obtained as a main reaction product, while the same mixture by the contact action of the same catalyst at higher temperature such as 350°, was noticed to be transformed into p-toluidine which was usually regarded as resulting from methylaniline by Hofmann reaction, and such transformation could not be observed to occur previously when alumina was used as the catalyst. In order to test whether the Hofmann reaction would occur actually by passing a mixture of aniline and methyl alcohol on the heated acid earth, 50 grams of the fourth fraction, b.p. 190–197°, shown in Table 3, which was composed of methylaniline, were passed again on the catalyst heated at 350°, and the reaction product was divided into the following 7 fractions, and the density of each fraction and the melting-point of the acetate, were studied, and also the primary amine-content by means of benzene sulphonylchloride.

TABLE 4.

No.	Fraction	Yield (gr.)	d_{20}^{20}	M.p. of acetate			RNH_2 %	N %
				1	2	3		
1	185–187°	5.5	0.9800	113–116°	96°	96–98°	—	9.50
2	187–190°	9.0	1.0050	119–122°	107–111°	96–98°	88.94	9.44
3	190–193°	2.3	1.0050	117–119°	96–98°	83–86°	96.04	9.21
4	193–198°	7.2	1.0023	119–121°	98–100°	70–72°	92.94	9.24
5	198–202°	10.4	1.0000	121.5–124°	101–103°	99–101°	86.90	9.56
6	202–208°	3.0	0.9951	126–129°	115–118°	83–86°	87.30	9.48
7	about 208°	—	—	128–131°	120–122°	91–94.5°	—	—
	p-toluidine	—	—	—	—	—	—	9.39
	aniline	—	—	—	—	—	—	10.37

The fractions 2, 3, 4, 5, and 6 were confirmed from their physical and chemical properties, as consisting mainly of p-toluidine, and the writer has succeeded in obtaining it in pure state as an acetate (m.p. 147°; N=9.40%) from the fifth fraction by fractional crystallisation. And analogously, the first and last two fractions were confirmed to contain chiefly of aniline and dimethylaniline respectively.

The writer, thus, has proved experimentally the assumption that methylaniline formed by the direct condensation of methyl alcohol and aniline, was transformed into p-toluidine by contact action of the acid

earth at higher temperature, with the formation of aniline and dimethylaniline.

The mechanism of the reaction for the formation of p-toluidine and dimethylaniline by the interaction of methyl alcohol and aniline in presence of the catalyst will be explained by the following scheme :

$$CH_3OH + C_6H_5NH_2 \longrightarrow C_6H_5NHCH_3 \longrightarrow CH_3C_6H_4NH_2 \cdots\cdots(1)$$

$$C_6H_5NH(CH_3) \longrightarrow C_6H_5NH_2 + C_6H_3N(CH_3)_2 \cdots\cdots(2)$$

Dimethylaniline which occurs in the reaction product of methylaniline by the contact action, and of aniline and methyl alcohol in presence of the acid earth, should behave in an analogous way yielding methyl-p-toluidine, methylaniline and xylidines, with methylaniline, by the contact action of the catalyst at high temperature.

70 grams of dimethylaniline which contains 4.7% of methylaniline as an impurity, were passed on the catalyst heated at 350°, and a reaction product composed of 35% of primary amines, 28% of secondary amines, and 37% of tertiary amines, was obtained which was divided into 9 fractions by distillation. Of each fraction, the density, content of primary amines, melting point of acetates and content of nitrogen were determined, and the results are shown in the following table.

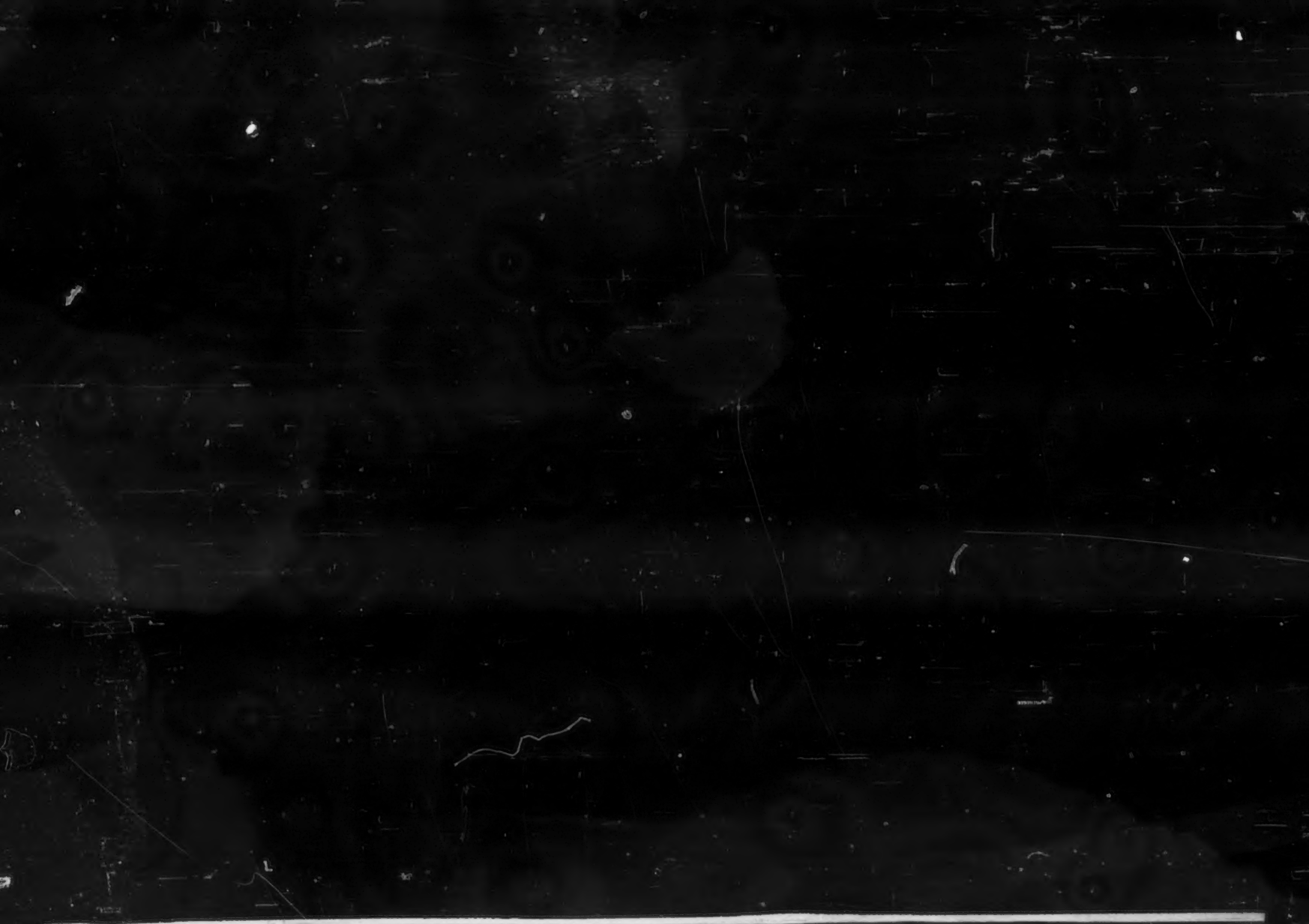
TABLE 5.

No.	Fraction	Yield (gr.)	d_{20}^{20}	R—NH_2 %	M.p. of acetate		Content of N %	
					1	2	1	2
1	140-195°	1.0	—	—	—	—	—	—
2	195-198°	7.0	0.9765	42.70	—	122-124°	9.05	—
3	198-201°	10.0	0.9749	40.98	130-131°	125-128°	9.14	—
4	201-203°	11.0	0.9746	39.42	138-141°	124-127°	9.29	8.77
5	203-205°	17.0	0.9734	37.84	134-135°	130-133°	9.29	8.11
6	205-207°	12.0	0.9704	31.43	139-142°	129-130°	9.16	8.27
7	208-210°	4.0	0.9686	27.26	138-141.5°	129-134°	9.28	7.90
8	211-215°	2.0	0.9686	—	94-96°	—	7.59	—
9	215-225°	2.9	—	—	103-105°	—	—	—

Content of nitrogen in the acetate of C_7H_9N 9.39%

" " " " " $C_8H_{11}N$ 8.58%

As will be seen in the experimental results shown in the table above, p-toluidine and methyl-p-toluidine composed chiefly the reaction product, and the chemical reactions for the formation of these compounds from dimethylaniline will be shown in an analogous manner to the transformation of methylaniline into p-toluidine and other amines.

The migration of the methyl radical in both the methyl- and dimethyl-anilines, from the nitrogen atom to the carbon atom, forming p-toluidine and methyl-p-toluidine, was effected by the contact action of Japanese acid earth, and such chemical change was found with silica but not with alumina, the both were considered to be principal constituents of Japanese acid earth.

Tokyo Imperial Industrial Laboratory,
Hatagaya, Tokyo.